THE ANALYST.

APRIL, 1894.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The usual Monthly Meeting of this Society was held on March 7th at the rooms of the Chemical Society, Burlington House. In the absence of the President, Mr. Alfred H. Allen took the chair.

The minutes of the last meeting were read and confirmed.

The following gentlemen were duly elected: As Members, Leonard Archbutt, Derby; B. E. R. Newlands, Mincing Lane; T. H. Pearmain, Apothecaries' Hall. As Associate, Raymond Ross, Worcester.

The following papers were read: "Notes from the Laboratory of the Royal Agricultural Society of England: (i.) The Occurrence of a Poisonous Leguminous Seed in Indian Peas; (ii.) Analyses of Waters from Wells in close proximity to Churchyards," by J. Augustus Voelcker, Ph.D., B.Sc. "Beef-Stearin in Lard," by Otto Hehner.

THE COMPOSITION OF MILK AND MILK PRODUCTS.

By H. Droop Richmond.

Read at the Meeting Februarg 7th, 1894.

This paper is a continuation of the annual reports of the work done in the laboratory of the Aylesbury Dairy Company. The results obtained during 1893 are given in the present communication. (For previous reports see Analyst, vii. 53; viii. 33; ix. 56; x. 67; xi. 66; xii. 39; xiii 46; xiv. 69; xv. 44; xvi. 61; xvii. 62; and xviii. 50.)

The total number of samples analyzed during the year 1893 was 30,504; this is a large increase, the numbers having gradually advanced year by year from 8,817 in 1881, when the company's laboratory was first established.

28,487	samples of	milk.
1,121	,,	cream.
624	,,	separated and skimmed milk.
13	,,	buttermilk.
122	,,	butter.
91	,,	water.
46	,,	sundry articles.

Of the milk samples, 14,643 were taken from the railway churns, on their arrival at the company's chief depôt. The bulk of this is distributed with the least possible delay to the customers, a certain portion being, however, utilized for the production

of cream, etc. To control the men employed in delivering the milk, a further 11,479 samples were taken, before, during and after delivery, and analyzed comparatively. In the following table the average monthly results of these analyses are given. The samples taken on arrival, before and during delivery, were almost exclusively analyzed by estimating the total solids and specific gravity, and calculating the fat. A large portion of those taken at commencement of and after delivery were, however, examined by the Leffmann-Beam method, and the total solids calculated. The agreement is equally good between the different series. No cases in which the milk had been tampered with were found.

AVERAGE COMPOSITION OF MILK DURING 1893.

1893.	On Arrival.				Before Delivery.	At Commencement of Delivery.	During Delivery.	After Delivery.
Month.	Sp. Gr.	Tot. Sol.	Fat.	S. n. F.	Tot. Sol.	Tot. Sol.	Tot. Sol.	Tot. Sol.
January	1·0321	12·68	3·85	8·83	12·50	12·60	12·68	12·71
February	1·0321	12·58	3·76	8·82	12·46	12·56	12·57	12·64
March	1·0320	12·52	3·73	8·79	12·46	12·52	12·52	12·60
April	1·0319	12·53	3·75	8·78	12·45	12·40	12·45	12·55
May	1·0319	12·46	3·70	8·76	12·42	12·37	12·40	12·61
June	1·0316	12·37	3·70	8·67	12·30	12·29	12·31	12·44
July	1·0311	12·41	3·83	8·58	12·31	12·35	12·25	12·39
August	1·0314	12·54	3·89	8·65	12·46	12·47	12·44	12·48
September	1·0316	12·80	4·06	8·74	12·64	12·63	12·62	12·66
October	1·0317	13·20	4·39	8·81	12·93	12·94	13·03	12·99
November	1·0321	13·09	4·21	8·88	12·90	12·91	12·96	12·90
December	1·0321	12·94	4·08	8·86	12·77	12·72	12·76	12·73
Average	1·0318	12·68	3·91	8·77	12·55	12·56	12·58	12·64

After the abnormal summer of 1893, one would have naturally expected to find that the milk this year was of poorer quality than usual; and it will probably be a matter of surprise that the yearly average of total solids is but 0·03 per cent. lower than that of last year, the amount of fat being absolutely identical with that of the past two years, the difference being only in the solids-not-fat. During the months of June, July and August the solids-not-fat were distinctly below the average, and this seems to have been the only effect of the season on the composition of milk. I have already shown (ANALYST, xviii. 270) that by careful examination it has been possible in many cases to distinguish between abnormal and watered samples, and have nothing further to add here on this subject. I may say that when the mixed milk of a whole farm has been examined during 1893, in but one instance has the fat fallen below 3·0 per cent., and in this one case it was 2·99 per cent. The experience of this year has gone to show that the Society's limit for fat is well fixed.

The highest percentages of total solids and fat occurred in October, and the lowest in June.

Cream samples were taken before and during delivery. The average of the results is given in the following table:

AVERAGE AMOUNT OF FAT IN CREAM DURING 1893.

Month.	Before Delivery.	After Delivery.
January	45·0	45·5
February	45·5	46·0
March	46·3	46·5
April	47·3	48·4
May	48·4	48·9
June	48·8	48·4
July	46·7	47·2
August	47·3	47·5
September ..	50·8	50·8
October	49·8	50·9
November	46·8	47·4
December	47·3	47·7
Average	47·5	47·9

Considering the difficulty of drawing average samples of cream of such richness, the agreement between the two series is satisfactory.

The average composition of clotted cream (51 samples) was as follows:

	Average.
Water	30·77
Fat	61·49
Ash	·60
Solids-not-fat	7·74

These figures do not greatly differ from those found in former years.

The bulk of samples of separated milk contained less than ·3 per cent. of fat; in rare instances it contained above ·4 per cent. The lowest amount of fat contained in skimmed milk was ·04 per cent.

Butter had the following composition:

French butter, fresh; 35 samples.

Water	15·53 to 11·12	; average	13·65
Fat	87·06 ,, 83·27	,,	84·99
Solids-not-fat ...	1·86 ,, ·86	,,	1·36
Salt	·25 ,, ·05	,,	·13
Reichert-Wollny figure	27·5 ,, 32·3	,,	30·2

French butter, salt; 28 samples.

Water	13·49 ,, 9·17	,,	11·61
Fat	88·07 ,, 82·74	,,	85·08
Solids-not-fat ...	4·83 ,, 2·32	,,	3·31
Salt	2·95 ,, 1·08	,,	1·86
Reichert-Wollny figure	27·5 ,, 33·0	,,	29·8

English butter, salt; 43 samples.

Water	15·33 to 10·28	average	12·76
Fat	87·24 ,, 82·25	,,	84·53
Solids-not-fat ...	3·94 ,, 1·16	,,	2·71
Salt	3·31 ,, ·59	,,	1·90
Reichert-Wollny figure	21·6 ,, 32·3	,,	28·1

Swedish butter, salt; 3 samples.

Water	14·36 ,, 13·10	,,	13·64
Fat	83·52 ,, 82·02	,,	82·96
Solids-not-fat ...	3·62 ,, 3·19	,,	3·40
Salt	2·36 ,, 2·07	,,	2·19
Reichert-Wollny figure	29·5 ,, 31·2	,,	30·5

One sample of English butter gave a Reichert-Wollny figure of 21·6 c.c.; this was churned at Bayswater, and duplicate determinations were made. This figure is not, however, lower than has been found by Vieth, Mayer, Lupton, and others.

For the discussion of the amount of water in butter, see ANALYST, xx. 16.

The Leffmann-Beam glycerol method has been exclusively used during 1893 for the determination of the volatile acids. It will be noticed this year that French butters give a higher Reichert-Wollny figure than English butters; reference to previous reports will show that this has been invariably the case.

A sample of butter which had been kept for two years exposed to air and light, and which Dr. Vieth had found when fresh to require 29·9 c.c. $\frac{N}{10}$ alkali to neutralize the volatile acids from 5 grammes, took 29·5 c.c. $\frac{N}{10}$ alkali.

Another sample received by Dr. Vieth from the German Commission on Butter Analysis in 1888, and which he has on several occasions analyzed (see ANALYST, xiv. 148; xv. 173), took 33·9 c.c. $\frac{N}{10}$ alkali, as against 32·0 c.c. originally.

A sample of milk was skimmed in three portions—*i.e.*, after six hours' standing, eighteen hours, and twenty-four hours. The last, very small quantity of cream on being churned into butter, took identically the same amount of $\frac{N}{10}$ alkali, 26·5 c.c., as the earlier portions. It seems that the larger and smaller globules of fat do not differ chemically.

The specific gravity of every sample of milk which comes into the laboratory is taken. This determination is of the greatest value, and, when taken with a lactometer, as is our practice, next to no trouble. Lactometers, which can be read to the fourth place of decimals with a little practice, are now made which require only 2 oz. or 4 oz. of milk. It must, however, be borne in mind that the specific gravity of milk cannot be accurately taken until the expiration of some hours after milking, for until this time, as Vieth has pointed out (ANALYST, xiv. 71), Recknagel's phenomenon is still going on.

An opportunity occurred this year of studying this. The following figures were obtained:

Specific gravity $1\frac{1}{4}$ hours after milking	1·0310
,, ,, $3\frac{1}{4}$,, ,, ,, ...	1·0322
,, ,, 18 ,, ,, ,, ...	1·0325

This rise in specific gravity must not be confounded with a similar rise in the observed specific gravity shown when frothy milk is allowed to stand; it is quite

independent, and is due to some change in the dissolved constituents of the milk. When milked, air-bubbles are always mixed with the milk, but these rise to the top in the course of an hour or less, leaving a very little froth on the top, which is very persistent, and must be removed before taking the specific gravity; occasionally it happens that a sample for analysis contains much froth, and great care must then be exercised in taking the specific gravity.

For very exact determinations of the specific gravity, a small (10 c.c.) Sprengel tube must be used; a bottle is inadmissible, as there is not time for the temperature to become equal throughout before some of the cream separates. With the Sprengel tube uniformity of temperature is reached in a few minutes, and accuracy to ·0001 is easily attained.

All exact determinations of total solids have been done by the asbestos method, and the results have been most satisfactory. Macfarlane's chrysotile (ANALYST, xviii. 73) method has also been studied, and the statement in his paper, that this method gives lower results than drying in a basin, confirmed.

It seemed to me that, as no figures were given as to whether the chrysotile could be dried to constant weight, and whether it gave anything to ether, it was desirable to examine into this point:

Weight of tube and chrysotile after 20 hours at 100° C. ...	16·266
,, ,, ,, ,, 5 ,, more	16·263

The tube was then wetted with 10 c.c. of water and dried:

Weight of tube and chrysotile after 19 hours at 100° C. ...	16·2675
,, ,, ,, ,, 2½ ,, more	16·264
,, ,, ,, ,, 17 ,, ,, ...	16·269
It was then extracted with ether, and on drying	16·263

No ether extract whatever was obtained.

The weighings, though not entirely satisfactory, show that chrysotile can be dried and re-dried to a fairly constant weight.

In three milks the total solids were estimated:

Chrysotile method ...	5 hours at 100° C.	13·00		
,, ,,	20 ,, ,,	12·63	12·85	
,, ,,	25 ,, ,,	12·63	12·82	12·77
Asbestos method in basin ...	,, ,, ,,	13·23	13·21	13·09
Difference		·60	·39	·32

In each case the chrysotile method was lower, and the residue was of a brown colour, while it was white in the asbestos method.

Fat was also estimated by the chrysotile method, and compared with the Adams method:

Chrysotile method—Fat, direct weighing ...	4·12	4·28	3·88
,, ,, ,, by difference... ...	4·13	4·27	3·91
Adams method	4·08	4·17	4·06

The tubes were percolated with ether about six times; in the first two cases a little chrysotile had run through, which makes the results high. There does not seem to be much difference between the two methods.

As the total solid determination does not compare with the methods used in

England, and, moreover, is probably low, as the residue is brown, this method is not likely to be adopted here.

Numerous comparisons between the Adams and Werner-Schmid methods were again made this year; the Werner-Schmid averaged ·03 higher than the Adams, and had a probable error of ±·041, the probable error of the Adams being ±·027.

This shows that the Werner-Schmid method is good enough for ordinary work; it has not, however, in my hands proved such a very rapid method, an hour and a half being the least time in which a satisfactory estimation can be performed. I find that it is necessary to allow the tube in which the dissolved milk and ether have been shaken up to stand *at least* ten minutes before drawing off the ether, as before that time the ether contains minute water globules, visible to the naked eye, and more easily seen with a magnifying glass. I have found it very difficult to prevent a slight loss of ether on taking out the stopper of the tube. I have now quite discarded this method for either the Leffmann-Beam centrifugal method, in case a rapid determination is wanted, or the Adams method, where accuracy is a desideratum.

In doing an accurate Adams estimation, attention to the following points is necessary:

i. The ether must be anhydrous (dried over calcium chloride and distilled is sufficient).
ii. Schleicher and Schüll's fat free papers should be used, and one should be extracted without any milk on it, in a flask used as a tare for the others.
iii. Four or five hours' extraction is necessary.
iv. The coils must be well dried before extraction.

Neglect of the first, second, and fourth precautions causes the results to be too high, and as one or more of these had been neglected in the data from which the formula of Hehner and myself, and my modified formula, were calculated, I thought it desirable to calculate a new formula.

The determinations were made as follows:

Specific gravity. By a Sprengel tube, frequently tared, at 15·55° C. (determined by a Kew standardized thermometer read to $\frac{1}{10}$° C.).
Total solids. Asbestos method.
Fat. Adams method, using the precautions enumerated.

The results are given in two series. In Series I. all determinations of total solids and fat are means of well agreeing duplicates; in Series II. some of the specific gravities were taken with a lactometer, and many of the total solid and fat determinations were not done in duplicate.

Series I. extends over an entire year, and the results are arranged in order of date; the importance of this will be realized later:

SERIES I.

	G.	$\frac{G.}{D.}$	T.	F.	F. calc.	Difference.	Remarks.	
1.	34·9	33·7	9·27	·28	·35	+ ·07		1st Period
2.	30·8	29·9	12·75	4·10	4·08	− ·02		,,
3.	33·5	32·4	12·88	3·70	3·65	− ·05		,,
4.	32·0	31·0	12·83	3·85	3·91	+ ·06		,,
5.	31·7	30·75	13·09	4·13	4·18	+ ·05		,,

	G.	$\frac{G.}{D.}$	T.	F.	F. calc.	Difference.	Remarks.	
6.	32·2	31·2	12·56	3·65	3·64	− ·01		1st Period.
7.	26·0	25·35	10·17	2·92	2·93	+ ·01		,,
8.	32·3	31·3	12·96	3·92	3·96	+ ·04		,,
9.	32·5	31·5	12·75	3·72	3·74	+ ·02		,,
10.	14·1	13·9	5·57	1·56	1·60	+ ·04		,,
11.	31·7	30·75	12·25	3·56	3·48	− ·08		,,
12.	32·0	31·0	12·48	3·66	3·63	− ·03		,,
13.	31·8	30·8	13·74	4·64	4·72	+ ·08		,,
14.	32·6	31·55	13·04	3·99	3·97	− ·02		,,
15.	25·8	25·15	10·06	2·93	2·88	− ·05		,,
16.	32·3	31·3	12·52	3·60	3·59	− ·01		,,
17.	32·4	31·4	12·58	3·65	3·62	− ·03		,,
18.	32·0	31·0	13·09	4·06	4·12	+ ·06		,,
19.	29·4	28·55	12·06	3·78	3·82	+ ·04		,,
20.	29·9	29·05	12·64	4·13	4·18	+ ·05		,,
21.	61·4	57·85	20·84	4·73	4·61	− ·12	Concentrated Milk.	,,
22.	36·0	34·75	11·68	2·06	2·13	+ ·07		,,
23.	32·8	31·75	12·44	3·48	3·42	− ·06		,,
24.	32·7	31·65	12·42	3·46	3·43	− ·03		2nd Period.
25.	32·6	31·55	12·41	3·51	3·44	− ·07		,,
26.	32·7	31·65	11·91	3·01	3·00	− ·01		,,
27.	32·5	31·5	12·32	3·46	3·38	− ·08		,,
28.	23·4	22·85	9·82	3·21	3·18	− ·03		,,
29.	33·2	32·15	11·86	2·92	2·86	− ·06		,,
30.	32·4	31·4	12·59	3·64	3·63	− ·01		,,
31.	32·7	31·65	12·51	3·61	3·50	− ·11		,,
32.	32·6	31·55	12·58	3·70	3·58	− ·12		,,
33.	32·8	31·75	12·62	3·67	3·58	− ·09		,,
34.	32·6	31·55	12·29	3·41	3·34	− ·07		,,
35.	32·4	31·4	12·25	3·49	3·35	− ·14		,,
36.	32·5	31·5	12·30	3·46	3·37	− ·09		,,
37.	32·5	31·5	12·30	3·52	3·37	− ·15		,,
38.	31·8	30·8	12·59	3·76	3·76	—		,,
39.	32·4	31·4	11·91	3·14	3·05	− ·07		,,
40.	32·3	31·3	12·27	3·48	3·38	− ·10		,,
41.	32·0	31·0	12·64	3·80	3·75	− ·05		,,
42.	30·9	29·95	11·34	2·88	2·90	+ ·02		,,
43.	32·1	31·1	12·60	3·65	3·70	+ ·05		,,
44.	32·0	31·0	12·16	3·35	3·35	—		,,
45.	32·9	31·85	11·97	2·85	3·01	+ ·16		3rd Period.
46.	31·6	30·65	12·51	3·67	3·72	+ ·05		,,
47.	31·6	30·65	12·62	3·77	3·81	+ ·04		,,
48.	32·1	31·1	12·39	3·40	3·52	+ ·12		,,
49.	32·0	31·0	12·42	3·44	3·58	+ ·14		,,
50.	32·1	31·1	12·14	3·21	3·32	+ ·11		,,
51.	32·1	31·1	12·06	3·19	3·25	+ ·06		,,
52.	32·6	31·55	11·74	3·00	2·88	− ·12		,,
53.	32·4	31·4	11·73	2·99	2·92	− ·07		,,
54.	31·0	30·05	11·95	3·31	3·38	+ ·07		,,
55.	31·5	30·55	12·36	3·51	3·62	+ ·11		,,
56.	31·4	30·45	12·30	3·52	3·59	+ ·07		,,

	G.	$\frac{G.}{D.}$	T.	F.	F. calc.	Difference.	Remarks.
57.	31·3	30·35	12·47	3·76	3·75	− ·01	3rd Period.
58.	31·3	30·35	12·53	3·77	3·80	+ ·03	,,
59.	28·7	27·9	9·72	2·05	2·00	− ·05	,,
60.	32·0	31·0	12·67	3·75	3·77	− ·02	4th Period.
61.	31·9	30·9	12·61	3·73	3·75	+ ·02	,,
62.	32·0	31.0	12·69	3·77	3·79	+ ·02	,,
63.	31·8	30·8	12·89	3·93	4·01	+ ·08	,,
64.	32·2	31·2	12·39	3·53	3·50	− ·03	,,
65.	32·2	31·2	12·42	3·49	3·52	+ ·03	,,
66.	33·3	32·2	12·84	3·64	3·66	+ ·02	,,
67.	33·3	32·2	12·82	3·59	3·64	+ ·05	,,
				Series II.			
68.	33·4	32·3	12·10	3·05	3·02	− ·03	
69.	31·5	30·55	11·54	2·85	2·93	+ ·06	
70.	7·2	7·15	32·50	25·67	25·55	− ·12	Carter Bell's Method.
71.	32·0	31·0	13·35	4·34	4·32	− ·02	
72.	33·0	31·95	13·23	4·08	4·03	− ·05	
73.	32·0	31·0	13·21	4·17	4·22	+ ·05	
74.	32·6	31·55	12·06	3·16	3·15	− ·01	
75.	32·6	31·55	13·07	4·08	3·99	− ·09	
76.	32·7	31·65	12·61	3·48	3·58	+ ·10	
77.	32·4	31·4	12·92	3·84	3·91	+ ·07	
78.	32·4	31·4	13·17	4·15	4·12	− ·03	
79.	33·5	32·4	11·83	2·76	2·77	+ ·01	
80.	31·6	30·65	15·40	6·19	6·12	− ·07	
81.	29·6	28·75	11·30	3·02	3·12	+ ·10	
82.	33·5	32·4	11·27	2·22	2·30	+ ·08	
83.	29·7	28·85	15·00	6·32	6·19	− ·13	
84.	32·3	31·3	12·68	3·76	3·72	− ·04	
85.	33·2	32·15	12·03	3·03	3·00	− ·03	
86.	33·3	32·2	12·44	3·35	3·32	− ·03	
87.	32·3	31·3	11·93	3·11	3·10	− ·01	
88.	31·2	30·25	11·30	2·98	2·80	− ·18	
89.	33·5	32·4	12·66	3·56	3·47	− ·09	
90.	34·2	33·05	12·93	3·68	3·55	− ·13	
91.	33·5	32·4	12·20	3·24	3·09	− ·15	
92.	33·5	32·4	11·83	2·79	2·78	− ·01	
93.	33·1	32·05	11·30	2·38	2·41	+ ·03	
94.	32·8	31·75	13·05	3·85	3·93	+ ·08	
95.	32·4	31·4	12·26	3·43	3·36	− ·07	
96.	31·5	30·55	12·71	4·02	3·91	− ·11	
97.	33·9	32·8	10·54	1·44	1·61	+ ·17	
98.	33·8	32·7	11·21	2·26	2·19	− ·07	
99.	32·9	31·85	12·41	3·39	3·37	− ·02	
100.	32·5	31·5	12·49	3·50	3·52	+ ·02	
101.	32·2	31·2	11·97	3·18	3·15	− ·03	
102.	32·1	31·1	12·13	3·26	3·31	+ ·05	
103.	32·5	31·5	12·04	3·06	3·15	+ ·09	
104.	28·9	28·1	15·01	6·21	6·36	+ ·15	
105.	33·5	32·4	11·27	2·32	2·31	− ·01	
106.	30·0	29·1	11·37	2·93	3·11	+ ·18	

	G.	$\frac{G.}{D.}$	T.	F.	F. calc.	Difference.	Remarks.
107.	33·0	31·95	11·49	2·65	2·58	−·07	
108.	32·0	31·0	12·24	3·51	3·42	−·09	
109.	30·5	29·6	12·14	3·64	3·65	−·01	
110.	32·5	31·5	11·68	2·82	2·85	+·03	
111.	28·0	27·25	10·63	2·72	2·90	+·18	
112.	29·4	28·55	11·84	3·50	3·62	+·12	
113.	28·6	27·8	11·62	3·53	3·60	+·07	
114.	35·6	34·4	11·64	2·26	2·18	−·08	
115.	33·3	32·2	10·57	1·60	1·77	+·17	
116.	36·0	34·75	9·45	·27	·27	—	

The formula deduced from these determinations was $T = ·2625\frac{G}{D} + 1·2\ F.$

It is hardly necessary to state that the maximum specific gravity was used in the calculation.

In this formula it has been assumed that the specific gravity of butter fat at 15·55° C. is ·93, and not ·94, which was deduced from previous work (*cf.* ANALYST, xiv. 121). A formula was also calculated using ·94 as the specific gravity of butter fat, but the agreement with this latter formula was not quite so good. It is evident that the figure ·94 is not accurate, though possibly it is correct for the fat extracted by the less accurate methods hitherto used.

The form of formula adopted assumes that the influence of 1 gramme of solids-not-fat dissolved in 100 c.c. is a constant—*i.e.*, that milk may be regarded as a mixture of water, fat and solids-not-fat. It is well known, however, that few substances con form absolutely to this law. To show that in milk this law holds with practical exactitude, I quote the results of an experiment performed some years ago, and published in a different form in THE ANALYST, xiv. 127.

A poor separated milk was diluted, and the total solids and specific gravity estimated in the various mixtures.

Total Solids per cent.	Specific Gravity at 15·55° C.	Influence of 1 grm. of Total Solids per 100 c.c. on Specific Gravity.
9·280	1·03544	3·688
8·758	1·03343	3·693
8·318	1·03170	3·694
7·777	1·02950	3·684
7·456	1·02829	3·690
6·455	1·02439	3·688
		Average 3·6895 ± ·0033

From the probable error of the methods used I calculate that the probable error should be about ·1 per cent. of the absolute value, while the probable error found is ·09 per cent. This shows that the law holds with milk within the limits of error of the methods of analysis.

In Series 1 I have divided the estimations into four periods—*i.e.*, November to

January, February to April, May to July, August to October—and I find the average error in each of these periods to be as follows :

$$1893 \begin{cases} \text{1st period} & — \\ \text{2nd} \quad ,, & -\cdot06 \\ \text{3rd} \quad ,, & +\cdot05 \\ \text{4th} \quad ,, & +\cdot02 \end{cases}$$

It is remarkable that, in the previous year, when the method was not quite the same and the milk scale was used, that the differences were :

$$1892 \begin{cases} \text{1st period} & — \\ \text{2nd} \quad ,, & -\cdot04 \\ \text{3rd} \quad ,, & +\cdot07 \\ \text{4th} \quad ,, & +\cdot02 \end{cases}$$

Whether the fact that fats calculate low in the spring and high in the summer be due to a difference in the composition of the milk, or some unknown external conditions, cannot be decided ; as practically the same differences have been observed for two successive years, it is probable that this is not a purely accidental occurrence, and it may reasonably be expected to occur again.

There is some evidence that it occurred in 1889, as I then calculated a formula $T = \cdot263\frac{G}{D} + 1\cdot17\ F$, using methods but little different from the present one, which gives results differing about ·07 to ·08 from the present one ; and the work on which this was based was all done in the spring—*i.e.*, in the second period.

In 135 samples of genuine milk the ash has been determined, and the ratio to 100 parts of solids-not-fat calculated.

Solids-not-fat.	No. of Samples.	Ratio of Ash to 100 Solids-not-fat.	
		Limits.	Average.
9·4	1		8·5
9·3	1		8·1
9·2	4	8·0—8·4	8·2
9·1	12	7·9—8·5	8·2
9·0	23	7·8—8·4	8·15
8·9	27	7·9—8·5	8·2
8·8	21	8·0—8·4	8·2
8·7	8	7·9—8·8	8·3
8·6	4	8·0—8·6	8·3
8·5	7	8·1—8·7	8·4
8·4	7	8·3—8·7	8·5
8·3	5	8·5—8·9	8·7
8·2	6	8·6—9·0	8·9
8·1	6	8·8—9·4	9·0
8·0	2	8·8—9·3	9·0
7·7	1		9·1

In all these cases the ash was determined with the utmost care, frequently in a muffle, but never at a temperature above a very dull red.

A considerable proportion of these have been found with an alkaline reaction to both turmeric and litmus paper, and phenolphthalein; in some the alkalinity has been determined, and a maximum amount of ·025 per cent., calculated as Na_2CO_3, has been found; in some samples a slightly fuller examination has been made.

No.	Soluble Ash.	Insoluble Ash.	Na_2CO_3.	P_2O_5.	CaO.	Percentages on Insoluble Ash.	
						P_2O_5.	CaO.
1.	·26	·54	·025				
2.	·24	·53	·010	·228	·166	43·0	31·3
3.	·28	·48	·020	·205	·152	42·5	31·7
4.	·23	·55	·012	·226	·132	41·1	24·0
	·23	·54			·125		23·1

The soluble ash contained only the merest traces of phosphates, less than ·005 per cent. P_2O_5; it consisted of chlorides of the alkalies, and the carbonates to which the alkalinity was due; the insoluble ash consisted of a double phosphate of the formula (Ca,Mg) (K,Na) PO_4, analogous to the carbonates, sulphates and borates of calcium, and the alkali metals. The figures calculated for a calcium potassium phosphate are: CaO 32·2 and P_2O_5 40·5, and for a calcium sodium phosphate, CaO 35·4 and P_2O_5 44·9.

In Nos. 2 and 3 the amount of magnesium was very small and was not estimated; in No. 4 the magnesium estimation was lost, but it was seen to be much larger than in the others.

It is well known that the ash of milk does not represent the salts present therein, but includes phosphoric acid, produced by the oxidation of the phosphorus of the casein, which displaces the carbonic acid formed on igniting the organic salts of milk. A very important paper by Söldner (*Landw. Versuchstat.* xxxv. 351), which has not yet been properly appreciated, has greatly elucidated our knowledge on the subject. He shows that the phosphates present in milk are to a certain extent acid phosphates, and to these in part is the acidity of milk (to phenolphthalein) due. Milk when fresh, and in many cases for some time after, reacts alkaline to litmus. Among the salts the presence of which is established in milk, and which react alkaline to litmus, are citrates and phosphates of the formula M_2HPO_4; the practice of calculating the acidity of milk to phenolphthalein as lactic acid is not, therefore, correct; and, indeed, milk freshly drawn has an acidity (calculated as lactic acid) of ·1 per cent., or more.

With reference to the presence of nitric acid in milk, when a cow has been dosed with small proportions of nitrates, I thought it desirable to definitely ascertain if the use of water containing nitrates would produce the same effect. After a considerable amount of trouble, I succeeded in obtaining samples of milk yielded by cows accustomed to drink water containing 18·0 parts per 100,000 of nitric acid (as N_2O_5); these samples gave a strong diphenylamine reaction. My previous failure to find nitric acid is due to the fact that it is a *sine quâ non* that the water on all the farms supplying the company shall be unpolluted, and therefore contain nitric acid in

only small amount, and that this provision is enforced is shown by the large number (91) of water samples analyzed.

A few experiments were made as to the loss of water experienced on keeping butter samples. A quarter-of-a-pound sample was taken immediately after churning and analyzed at once, the sample was then kept under various conditions and reanalyzed.

As examples I may quote :

Fresh samples,	14·64 %	of water ;	after two days	in an open basin,	12·12 %
,, ,,	14·87 ,,	,,	,,	ten days wrapped in single paper,	13·99 %
,, ,,	13·10 ,,	,,	,, ,, ,, ,,	double ,,	11·93 %

With a view of studying the connection between the quality of milk yielded by cows and external conditions, I have noted this year the temperature of the air, and I find that it is a general rule that sudden rise of temperature causes a milk of poorer quality to be produced, while a sudden fall has the opposite effect ; should, however, the temperature continue low or high, the quality of the milk gradually returns to its normal level.

There seems to be some evidence that the quality of milk is improved by changing the food from time to time, but that the effect on the quality of the milk is not permanent. The fact that a change is made in the food seems to have more effect than the particular food given ; the evidence on this point is, however, by no means conclusive.

It is usually accepted as a fact that cream contains a larger proportion of solids-not-fat to water than the milk from which it was derived ; and the increase of solids-not-fat is said to be due to the fat globules taking up a larger amount of proteids than the proportion deduced from the ratio of proteids to water in milk. This has been used as an argument as to the presence of an albuminous membrane round the fat globules. I have, however, been led to doubt that this is the case, and have obtained results which point to the ratio of solids-not-fat to water, being the same in cream as in the milk from which it is derived.

The method of analysis which I adopt has been previously described by Dr. Vieth (Analyst, xvi. 1), but as it will be necessary to discuss one or two points, I describe it again in more detail. The sample for analysis is well mixed, and about 5 grammes are weighed into an eight-ounce, flat-bottomed, conical flask ; this is placed in an air-bath at 100°, and is shaken slightly at intervals of fifteen minutes till it is apparently dry, which takes about one hour ; it is then placed on its side, so that the fat shall run away from the solids-not-fat, and left in the air-bath for about four hours. I find that drying beyond this time does not decrease the weight, but rather increases it. A second portion, of 3 to 4 grammes, is placed in a platinum basin, and this is left in the air-bath for five hours, when the minimum weight is obtained. The two results have only differed by more than ·1 per cent. in two cases out of forty—viz., ·11 per cent. and ·25 per cent. The sample in the basin is used for the ash determination ; the flask is partially filled with ether (about 30 c.c.), and this is gently boiled, and allowed to stand for fifteen minutes and decanted, a second quantity of ether is then poured in, and the flask corked and allowed to stand till the following day, during which about six more washings with ether are performed. It

is then allowed to stand again for a night, and a further two or three washings are given; the solids-not-fat are then dried to constancy (about four hours) and weighed. In a few cases the ether has been evaporated and the fat weighed; the weights of the fat and the solids-not-fat do not differ by more than a milligramme or two from the weight of the total solids. In some cases the solids-not-fat have been ground up with a small pestle in the flask, and the ether filtered through a small tared filter; but I do not find that this method is much better than the other. In some cases the fat has been estimated by the Adams or Werner-Schmid methods, and the fat estimated this way and the solids-not-fat add up slightly below the total solids.

The reason for this is not far to seek. I heated in the same bath about 2 grammes of anhydrous butter fat (*i.e.*, shaken with a considerable proportion of calcium chloride at about 50° C. and filtered); the heating was continued for six days, but I need only quote one or two results here:

Time of Heating.	Percentage on Original.
1½ hours	100·17
16½ ,, ...	100·73
20½ ,, ...	100·81

As cream contains, say, 50 per cent. of fat, the increase on heating four to five hours will not be quite negligible, and may be estimated at ·1 to ·2 per cent. on the weight of the cream; and therefore the solids-not-fat determined by the difference between total solids estimated by drying for a long period, and fat estimated by methods in which the drying at 100° C. does not exceed fifteen to twenty minutes, will be increased by this amount.

In the method that I have adopted, there is a possibility that the extraction is not quite complete; and, on the other hand, though the greatest care was exercised in decanting the ether, it being done over a black surface, so that any solid particles going away with the ether might be seen, there is a possibility of loss in this way. I was, however, not able to observe any deposit in the decanted ether.

In the following analysis, the solids-not-fat have been calculated on the assumption that the ratio of the solids-not-fat to water was 10·2 to 100, which I have found to be the mean proportion in the milk which is generally used for the production of cream, except in No. 2, which was prepared by the shallow setting system, and the milk previously submitted to analysis, the ratio being 10·0 to 100; all the other creams were separated:

No.	Total Solids.	Solids-not-Fat.	S. n. F. Calculated.	Difference.
1. ...	32·50 ...	6·83 ...	6·90 ...	+·07
2. ...	37·59 ...	6·14 ...	6·24 ...	+·10
3. ...	50·92 ...	5·02 ...	5·01 ...	−·01
4. ...	55·05 ...	4·65 ...	4·59 ...	−·06
5. ...	55·18 ...	4·77 ...	4·57 ...	−·20
6. ...	55·97 ...	4·47 ...	4·49 ...	+·02
7. ...	56·37 ...	4·40 ...	4·45 ...	+·05
8. ...	57·99 ...	4·17 ...	4·28 ...	+·09
			Average Difference ...	+·01

In one cream, No. 1, a proteid estimation was made, and 2·60 per cent. was found, or 38·1 per cent. on the solids-not-fat. The mean proportion of proteids to the solids-not-fat in milk is, according to my estimate, 38·6 per cent.

The ash has also been determined, and the results compared with that calculated on the assumption that it is one-twelfth of the calculated solids-not-fat:

No.	Ash.	Ash Calculated.	Difference.
1.	·57	·57	—
2.	·52	·52	—
3.	·42	·42	—
4.	·38	·38	—
5.	·39	·38	−·01
6.	·38	·37	−·01
7.	·38	·37	−·01
8.	·41	·36	−·05

Except perhaps in the last case, the agreement is everything that can be desired.

As lack of time has prevented my making as extensive a series of determinations as might be desired, I cannot say that the statement that cream contains a higher proportion of solids-not-fat than milk is incorrect, but the whole of the evidence that I have obtained points in the direction contrary to that generally assumed. It seems probable that this statement arose from the fact that solids-not-fat determinations were made by difference, the total solids being too high, from an increase of weight of the fat on drying, and the fat possibly too low, owing to a method which gives an incomplete extraction being used (*e.g.*, Soxhlet's method), which I have shown, and Vieth has confirmed my observation, to give too low results. Cf. ANALYST, xiv. 123; and xvi. 203.

I have dwelt at length on this subject, as, were it true that cream contained a higher proportion of proteids, a field of investigation would be open to see if the corresponding deficiency of proteids might be utilized in the detection of separated milk as an adulterant; but I have now little hope of such being the case, and indeed, in a few experiments, I have found no deficiency of solids-not-fat or proteids in separated milk.

An analysis of the slime found on the inside of the drum of a cream separator has been made; its composition was:

Total solids		33·76		
Fat		·50		
Milk-sugar	(about)	·50		
Casein (or analogous body)	,,	22·00		
Ash		3·01		
Soluble ash	·166	containing	Cl	·008
Insoluble ash	2·844	,,	Silica	·171
			$Fe_2O_3Al_2O_3$	·012
			CaO	·654 = ·675 eq.
			MgO	·225 = ·325 eq.
			Alkalies	·559
			P_2O_5	1·233 = 1·506 eq.

The portion returned as casein was that part soluble in dilute alkalies and precipitated by acids. The "silica" was the portion insoluble in hydrochloric acid on evaporation. It is seen that the insoluble ash (minus silica, iron oxide, etc.) has the same general composition as the insoluble ash of milk (see *ante*)—*i.e.*, (Ca,Mg) (Na,K) PO_4.

There are 1·506 equivalents of P_2O_5 (1 eq. $= \frac{71}{3}$) for each equivalent of CaO and MgO present (1 eq. CaO $= \frac{56}{2}$, 1 eq. MgO $= \frac{40}{2}$), and this fact alone furnishes a strong argument that this slime is not (though it contains) the dirt in the milk, and that it is a true milk product.

The ash was absolutely neutral (litmus and phenolphthalein) in reaction.

Discussion.

Mr. Otto Hehner said that Mr. Richmond had extracted much interesting matter from a subject which had been very often discussed before. Sooner or later the Law Courts would have to decide the question as to whether butter was a perishable article or not. For the purposes of analysis, butter could hardly be called a perishable article, as it could be reliably analysed when many months old. Much of the confusion that had arisen from the conflicting statements of different observers—some of whom said that the percentage of insoluble fatty acids would not materially alter on keeping the samples, others that they decreased—was due to the fact that some analysts kept the butter entire, others the butter-fat. He was surprised that Mr. Richmond had not found any carbonates in his milk-ashes. He would rather have expected that there would have been a notable quantity. In sweetened condensed milks a deposit was generally observed, which consisted largely of calcium citrate, and which yielded on incineration calcium carbonate. He [Mr. Hehner] would like Mr. Richmond to state the lowest solids-not-fat which he had obtained.

Mr. Richmond, in reply, said that he could hardly give Mr. Hehner the lowest solids-not-fat, because the samples, which he believed were perfectly genuine, were not samples which were strictly authenticated in the legal sense. All the samples low in solids-not-fat were, however, abnormal in composition. With regard to the absence of carbon dioxide in the ash of separator-slime, it was not exactly the same thing as in the case of the deposit found in condensed milk, because it should be remembered that the condensed milk had been heated to a certain degree, and calcium citrate was known to be more insoluble in hot water than cold. In the ash of milk itself there was a small quantity of carbonic acid in a considerable number of cases. He had mentioned that in the soluble ash there was sometimes carbonic acid to the extent of 0·025 per cent. $NaCO_3$, and beyond that there was also a little carbonate in the insoluble ash. With respect to Mr. Hehner's remarks as to how difficult it was to wash milk-ashes, he thought a very possible explanation was that the alkali existed there as calcium-sodium-carbonate. He wished to mention that although the paper was in his name, the bulk of the analytical figures were the work of his assistant, Mr. Boseley.

[Note.—In a recent number of the *Comptes Rendus* there is a paper on the preparation of double carbonates of potassium and sodium with calcium, barium, and strontium, and they are described as well-defined crystalline compounds of limited solubility.—H. D. R.]

NOTE ON THE DETECTION OF COTTON-SEED OIL IN LARD.

By E. J. Bevan.

Read at the Meeting, February 7, 1894.

Some time ago I had occasion to examine a sample of lard for cotton-seed oil. This lard, which I knew to be genuine, gave the silver reaction. On finding this, the first thing I did was to make a new silver solution, but I found that the sample gave the reaction with all the solutions tried. It so happened that the bottle containing this lard had been long exposed to the air and the fumes of the laboratory. This gave me a clue to the matter. By scraping off the top portion, and taking a part of what lay underneath to which the air had not penetrated, I obtained no silver reaction whatever. I then took a sample of bladder-lard, and I observed the same phenomena. The portion immediately under the skin gave the silver reaction readily, whereas a portion taken right inside the mass in the bladder gave no reaction whatever. The fact that the lard underneath the skin gave the reaction showed, of course, that it was not due to the presence of any mechanically-deposited dirt. Then I tried exposing the lard in a still room in flat dishes. I found that after about a week's exposure the lard gave the silver reaction quite strongly. I can come to no other conclusion than that the effect observed was due to oxidation. I should say that I also exposed the lard to the fumes of various substances without afterwards obtaining any silver reaction whatever. I passed air for two or three days through some melted lard, and I found that with the lard so treated the reaction was intense. I estimated the amount of iodine absorption, the free acid, and one or two other things, and found no differences whatever, so that evidently the substance which is formed must be very minute in amount, but there is quite enough to mislead one, and give one the impression that cotton-oil is really present.

I notice that in the January number of the journal of the Chemical Society there appears an abstract of a "Note on the Reducing Action of Rancid Fat." It is stated by the author of that note that butter which has become rancid gives the cotton-seed oil reaction in a marked manner, and he also goes on to say that he considers the reaction to be due to the presence of sulphur compounds in lard, like those in certain vegetable oils. I do not think that this is true. It is known that lards do not contain sulphur compound. I cannot see that the effect is due to rancidity.

Mr. Chattaway said that it seemed to him strange that if the presence of free acid was in any way the cause of what Mr. Bevan had demonstrated, one should not get the reaction with the fatty acids themselves. He had very frequently tested fatty acids, and obtained no silver reaction.

Mr. Otto Hehner said that rancidity was not solely due to liberation of fatty acids, but was largely attributable to oxidation. Rancid fats, when saponified with alcoholic potash, gave a more or less yellow solution, similar to that produced when alkalies acted upon aldehydes; his impression was that rancidity was accompanied by the formation of aldehydic bodies. Mr. Mariani had pointed out that rancidity might cause butter-fat to yield a reaction with silver nitrate similar to the Becchi reaction. He (Mr. Hehner) advised members not to put too much trust in the cotton

seed oil reaction when applied to butter, as he had found that when cows were fed with large quantities of cotton-seed cake, the butter obtained from the milk of cows so fed would not unfrequently give the reaction for cotton-seed oil.

He would like to elicit from members some information concerning lard. A few years ago, when cotton-seed oil was frequently present in lard, the iodine absorption was largely relied upon in lard-testing. Lately, cotton-seed oil was but very rarely met with in lard, yet the iodine absorption had, if anything, increased, although beef-stearin, which had a very low iodine number, was often present. Hence the presence of some oil other than cotton-seed or lard oil must be suspected.

Mr. Cassal drew Mr. Bevan's attention to the fact that according to the abstract of Mr. Mariani's paper in the journal of the Chemical Society he appeared to have stated that he had shown lard and animal fats to contain sulphur compounds, and to have based that statement upon his having obtained the silver reaction with these fats, and upon his having found the deposit to consist partly of sulphide of silver.

Mr. Richmond, with respect to the presence of sulphur in the fat of animals pointed out that when he was in Egypt he examined the milk of the gamoose, and in the fat there was 0·05 per cent. of sulphur, and it gave, after saponification, a very strong reaction with both silver and lead paper. He thought it possible that, as sulphur was present in the fat of one animal, it might also be found in that of others.

Mr. Bevan said that he had only read the passage casually, but it seemed to him that there was not sufficient evidence upon which Mariani could base his statement.

CIDER VINEGAR.

By George S. Cox.

In connection with the enforcement of the Wisconsin vinegar laws (which require the presence of 4 per cent. of acetic acid and of 2 per cent. of solids in cider vinegar), the writer has spent some little time in the examination of these lines. In The Analyst for 1891 (p. 41) Mr. G. Embrey presents a paper devoted mainly to the consideration of the percentage of ash in cider. Upon reviewing some of the work done in the State laboratory the past summer I find some figures that may be of interest to your readers, taken in connection with Mr. Embrey's paper.

Mr. Embrey finds the ash to range from 0·25 per cent. to 0·35 per cent., a figure lower than 0·25 per cent. carrying the assumption of added water; but in regard to a figure higher than 0·35 per cent. no statement is made. On p. 42 is a criticism of R. Kayser's figures as quoted by Allen in his "Commercial Organic Analysis." Kayser gives the total solids of must as 16·25 per cent. and of cider as 2·36 per cent. The sugar of the former is given as 12·5 per cent. and of the latter as 0·75 per cent. Mr. Embrey says: "There is evidently some mistake here, as the total solid matter of cider is given as 2·36 per cent.—probably 12·36 per cent." The fact is here overlooked that the must has a high sugar content that has been removed from the cider by fermentation. With the trade in this country, the product of the cider mill and press is called "juice" before fermentation and "cider" after, and from the context of this

paper this same practice seems to obtain in England. In accordance with this, Kayser's figures are certainly more nearly correct that 12·36 per cent.

The table here given requires some additional explanation in addition to the remarks. 601, 602, 603, and 607 were samples of vinegar that had been made by the quick process in Gould generators. The other vinegars were made by storing the juice in barrels in a dark warehouse at a moderately warm temperature, and the dates mentioned refer to the time at which barrels were placed in storage. 626, 629, 630, and 631 were samples of juice pressed in 1893 (November), and examined within a few days after their manufacture. 608 to 620 inclusive the writer withdrew from the barrels in which it had been stored. The samples of juice were furnished by the manufacturer of the vinegars, and are just as represented.

Sample number.	Article examined.	Percentage of acid as acetic.	Percentage of total solids.	Percentage of ash to total amount.	Percentage of ash to total solids.	Remarks.
601	Vinegar	4·47	2·4	0·25	10·41	
602	,,	4·92	3·1	0·25	8·06	
603	,,	5·45	4·0	0·26	6·50	
604	,,	5·79	1·64	0·31	18·90	J. Put away in brls. in Oct., 1891.
605	,,	7·56	1·54	0·34	22·08	J. Put away in brls. but a few weeks earlier.
606	,,	6·09	2·29	0·36	15·72	J. Same date. Made from snow apples.
607	,,	5·29	2·43	0·259	10·65	
608	,,	7·74	1·77	0·435	24·57	J. Oct., 1891. Apples.
609	,,	6·19	2·17	0·40	18·43	J. Oct., 1891. Port wine brl.
610	,,	7·29	1·34	0·52	38·80	Ditto.
611	,,	8·40	2·66	0·39	14·66	J. Oct., 1891. Charred whisky brl.
612	,,	7·86	2·55	0·35	13·72	Ditto.
613	,,	6·19	2·23	0·34	15·24	Ditto.
614	,,	2·91	1·89	0·33	17·46	Put in warm storage. Fall of 1892.
615	,,	3·78	3·17	0·26	8·20	Ditto.
616	,,	7·81	1·43	0·33	23·07	November apples. 1891.
617	,,	5·32	2·74	0·43	16·42	Emptyings of brls. Three years old.
618	,,	2·28	2·09	0·30	14·35	November apples. 1892.
619	,,	5·63	1·55	0·30	19·29	November apples. Larger bung.
620	,,	8·09	2·27	0·40	17·62	Eight years old.
626	Juice	—	14·83	0·525	3·54	Solids dried twelve hours.
629	,,	—	13·36	0·286	2·14	New York apples ; not very sound.
630	,,	—	11·25	0·331	2·94	Partly fermented salicylic acid present.
631	,,	—	9·48	0·563	5·93	Same as 630, but from a vinegar barrel.
632	Settlings	—	2·54	0·246	9·68	Settlings from cider brls.

The average ash for the twenty-five samples is 0·3546 per cent.—a trifle higher than Mr. Embrey's maximum figure—and in only one instance (632) does the figure fall below the minimum; and certainly the settlings cannot be taken as a representative sample.

In samples 626, 629, 630, and 631 the solids were obtained after twelve hours drying on a steam bath. The evaporations were made in flat-bottomed platinum dishes, quite shallow and very thin.

The enforcement of this vinegar law has occasioned some very vexatious questions, and the Wisconsin Commission has given some little time to its consideration. Other points of interest present themselves in addition to the ash figures. Several of these vinegars cannot be sold, under existing statutes, as cider vinegar, while 603 could be watered very considerably and pass our State standard. Mr. Embrey's ash figures would prove little, as the ash is practically the same in 601, 602, and 603, yet the ratio maintained between the solids and acid would point to the addition of water. The goods were from the same place, in the same consignment, and were billed as 5 per cent., 4·5 per cent., and 4 per cent. acid strength respectively, and were evidently mixed with water in proportion to approximate the desired acidity. 618 and 619 were from the same run of juice, and stood side by side. They were examined eleven months after pressing, and are interesting as exhibiting the marked effect of a slight variation in the air-vent. 604, when received, contained nearly 4 per cent. by volume of alcohol that had not yet been converted, and the sample, in a half-gallon bottle, together with 605 and 606, was placed in the direct sunlight in a warm room, where it was allowed to stand for several months. The two other samples had little or no unconverted alcohol, and were practically unchanged, while 604 developed a bouquet and flavour incomparably superior to the others. Previously they had been stored in the dark and at a lower temperature, and when received were very similar in taste and odour, but the sunlight and warmth toward the close of the acetic fermentation created a difference that cannot be lightly estimated, from the commercial standpoint, at least.

Experiments upon this line are now in progress, and should anything of interest occur I shall be very glad to give you notes regarding it in a future contribution.

Wisconsin Dairy and Food Commission,
Madison, Wis., U.S.A.

NOTE ON G. S. COX'S PAPER ON CIDER-VINEGAR.

By A. H. Allen.

Mr. Cox's results are far more suggestive when calculated on the "original solids" of the apple-juice, and many of the anomalies disappear. The ratio of the ash to the residual solids of the vinegar has little meaning or interest, but the proportion it bears to the "original solids" of the juice before fermentation affords much assistance in forming an opinion as to the extent to which dilution has been practised.

The following table shows the "original solids" of Mr. Cox's samples calculated by Hehner's formula, and the ash for 100 parts of these solids. In calculating the

original solids of Sample 604 the alcohol present must be taken into consideration. But the correction I have applied is evidently excessive.

Sample Number.			Original Solids, per cent.	Ash on Original Solids, per cent.
601.	Vinegar		9·10	2·74
602.	,,		10·48	2·38
603.	,,		12·17	2·13
604.	,,		16·00	1·94
605.	,,		12·88	2·63
606.	,,		11·42	3·15
607.	,,		10·36	2·50
608.	,,		13·38	3·25
609.	,,		11·45	3·49
610.	,,		12·27	4·23
611.	,,		15·26	2·55
612.	,,		14·34	2·44
613.	,,		11·51	2·95
614.	,,		6·75	4·88
615.	,,		8·84	2·94
616.	,,		13·14	2·51
617.	,,		10·72	4·01
618.	,,		5·51	5·44
619.	,,		9·99	3·00
620.	,,		14·40	2·78
626.	Juice		14·83	3·54
629.	,,		13·36	2·14
630.	,,		11·25	2·94
631.	,,		9·48	5·93

THE DETERMINATION OF IMPURITIES IN COMMERCIAL COPPER.

By Bertram Blount.

The method given by Professor Hampe (*Chem. Zeit.*, 1893, xvi, 1691, see abstract on next page) depending upon the precipitation of the copper as cuprous thiocyanate and the determination of the metals present as impurities in the filtrate, has been in constant use in my laboratory for some years past, having been devised by me without knowledge of its previous employment.

The principle of the process is identical with that adopted by Professor Hampe, but there are a few differences in detail which add somewhat to its convenience. In most cases 10 grammes of the copper to be analysed is sufficient to yield ponderable quantities of the impurities to be determined, although of course this quantity may be increased if necessary. In fact, the great merit of the method consists in the fact that large quantities of material may be used without the trouble of handling unwieldy precipitates, as when once the copper has been precipitated as thiocyanate nothing further has to be done to it in the way of manipulation. When first working the process, I was accustomed to use 10 grammes of the copper and wash the resulting thiocyanate. This plan was speedily abandoned in favour of that mentioned by Professor Hampe, of drawing off a definite portion of the supernatant liquor and allowing for the volume occupied by the precipitate. In order to do this, it was

necessary to ascertain the specific gravity of cuprous thiocyanate. This constant was not given in any book which I consulted, and accordingly was determined on a sample prepared in the course of one of the previous analyses. The figure thus found for the specific gravity of cuprous thiocyanate at 15° C. compared with water at the same temperature, was 2·846, somewhat lower than that found by Professor Hampe (2·999). The reason for this discrepancy may be that the precipitation was conducted under different conditions which had an influence on the density of the salt. Taking the figure for the specific gravity of cuprous thiocyanate given above, a simple calculation showed that if 13·215 grammes of copper were taken, dissolved, precipitated as hiocyanate, and the solution together with the precipitate made up to 1 litre, on drawing off 750 c.c. the impurities corresponding to 10 grammes of copper would be obtained. By using this plan, all need for calculation of the results of the analysis is avoided.

Another point in which my process differs from that of Professor Hampe is that the copper is dissolved in aqua regia instead of nitric and sulphuric acids. By the use of this solvent, and the subsequent removal of the excess of nitric acid, I obtain a clear solution with all ordinary samples of copper, and avoid the necessity for making a separate analysis of the insoluble residue, a result which is, I venture to think, a distinct advantage. Thus all the common impurities of commercial copper, with the exception of gold, silver, sulphur, and oxygen, can be determined in one and the same solution, in the absence, moreover, of all but traces of copper, making the analysis a vastly simpler task than by the older methods.

There is only one other matter that deserves mention. Although arsenic can be determined in the solution from the cuprous thiocyanate, I have found it more expeditious, easy, and accurate to estimate it on a separate portion by distillation with ferric chloride and hydrochloric acid, as it is thus finally obtained as pure arsenious sulphide, and can be conveniently weighed in this form. There is only one drawback to this process, and that is the difficulty of obtaining reagents free from arsenic, making it necessary for the chemist to prepare them himself.

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The Determination of Foreign Metals in Commercial Copper. W. Hampe. (*Chem. Zeit.*, 1893, xvii. 1691-1692.)—The following is the method adopted by the author: 25 grammes of the sample are dissolved in a mixture of 200 c.c. of water, 100 c.c. of pure concentrated sulphuric acid, and 45—46 c.c. of nitric acid of sp. gr. 1·21. The quantity of the last-named reagent is reckoned so as to afford a small excess over that necessary for the oxidation of the quantity of copper taken, while the amount of sulphuric acid represents a considerable surplus, in order to prevent the separation of basic salts of bismuth and antimony when the solution is subsequently diluted. When the whole of the copper is dissolved, the solution is diluted with 200 c.c. of water to prevent the formation of crystals of copper sulphate. The resulting liquid is generally clear, but it may be turbid from the separation of insoluble antimoniates of copper and bismuth, which must in that case be filtered off and examined separately. The original solution, or the clear filtrate, as the case may

be, is warmed to 40° C., and treated with sulphur dioxide in a rapid stream to decompose the remainder of the nitric acid, the reduction being complete in about half an hour provided the temperature specified, which is the most favourable for the reaction, be observed. The solution, which should smell of sulphur dioxide, may be turbid from the presence of metallic silver precipitated by the reducing agent. Should it be desired to determine the silver in the wet way, the precipitation of traces not reduced by the sulphur dioxide is effected by the addition of a few drops of hydrochloric acid and the mixed precipitate of silver and silver chloride filtered off, converted completely into chloride and weighed in the usual manner. If, on the other hand, a dry assay for silver is to be made, the turbidity due to the separation of metallic silver may be disregarded, and the main body of liquid, together with the trace of metallic silver, is transfixed to a two-litre flask and precipitated with pure potassium thiocyanate, a rapid stream of sulphur dioxide being meanwhile maintained. A slight deficiency of potassium thiocyanate is used, so that a small fraction of the copper may remain in solution. The solution of potassium thiocyanate is of such strength that about 500 c.c. are required to precipitate 25 grammes of copper. The total bulk is then made up to two litres, the precipitate allowed to subside and a known volume of the supernatant liquor filtered off. 1800 c.c. is a convenient amount to take. The excess of sulphur dioxide is driven off by evaporation, and the foreign metals originally present in the copper, such as antimony, arsenic, bismuth, tin, iron and nickel, are separated and determined by the customary analytical methods. In making the calculations of the analysis it is necessary to correct for the volume of the cuprous thiocyanate in order to ascertain with what fraction of the 25 grammes of copper originally taken the quantity of liquid drawn off after precipitation corresponds. This involves a knowledge of the specific gravity of cuprous thiocyanate. The author has determined this value, and finds it to be 2·999, so that the volume occupied by the cuprous thiocyanate from 25 grammes of copper is 15·98 c.c. The total bulk of liquid in the two-litre flask may therefore be taken as 1984 c.c., and the relation between this number and that of the liquid drawn off, viz., 1800 c.c., determines upon what fraction of the 25 grammes of copper the estimation of foreign metals has been effected. Test analyses of pure copper, to the solution of which known quantities of impurities had been added, prove the accuracy of the method.

B. B.

The Separation and Volumetric Estimation of Lead. Lindeman and Motteu. (*Bull. Soc. Chim.*, 1893, x. 812, through *Chem. Zeit.*)—The authors have found that chloride of lime is capable of acting on native sulphides, converting their metals into oxides or peroxides and their sulphur into sulphate. The oxidation appears to be complete, and thus can be utilised for the estimation both of the metal and sulphur. In the case of galena the lead is obtained as peroxide, and can be estimated iodometrically. The analysis is performed by rubbing down 0·5 to 1·0 gramme of the sample in an agate mortar with a few drops of a solution of chloride of lime, and finally triturating the product with 30 to 40 c.c. of the same reagent. A little hydrochloric acid is then added, and the whole warmed until chlorine ceases to be evolved. The solution is diluted, and the lead peroxide washed by decantation, bringing as little as possible upon the filter, and treated with potassium iodide and hydrochloric acid; the liberated iodine is titrated with hyposulphite. The presence

of either iron or copper interferes, as each is capable of liberating iodine and is therefore reckoned as lead. When iron alone is present it is sufficient to precipitate the lead as sulphide with sulphuretted hydrogen in acid solution, and treat the sulphide as if it were the original ore. When copper has to be removed, the sulphide is precipitated as described above, and washed with potassium cyanide, which dissolves the cupric sulphide and leaves the lead sulphide to be dealt with as before.

B. B.

The Determination of Phosphoric Acid by the Titration of the Yellow Precipitate with Standard Alkali. (*Jour. Franklin Inst.*, 1893, cxxxvi., 362-376.)—The author shows that 23 molecules of sodium carbonate are required to neutralize the molybdic acid in every molecule of the yellow precipitate when the composition of this is $6NH_4.P_2O_5.24MoO_3$. The best standard alkali for the purpose is a solution of caustic potash, of which 1 c.c. is equivalent to 1 milligramme of P_2O_5 in the yellow precipitate. Such a solution neutralizes normal acid in the proportion of 100 : 32·65 volumes, and may be made from potash which has been freed from carbonate by means of baryta-water, on this basis; or it may be standardized by titration of the yellow precipitate obtained from pure sodium phosphate, treated in the manner described below.

The ammonium molybdate solution is prepared by dissolving 90 grammes of the salt in somewhat less than a litre of water, allowing the solution to settle, and decanting the clear liquor into a litre flask. The small quantity of insoluble molybdic acid always present is dissolved in a little ammonia, and added to the main solution. If the molybdate contains a trace of P_2O_5, a few decigrammes of magnesium sulphate, and ammonia to faint alkalinity, are added. The whole is then made up to one litre. Each c.c. precipitates 3 milligrammes of P_2O_5.

The standard acid must be equivalent to the alkali, and may be made by adding 326·5 c.c. of normal acid to one litre.

The analysis is conducted as follows: One gramme of phosphate rock, or 2 or 3 grammes of fertilizer, are dissolved in nitric acid, and, without evaporating to dryness, diluted to 250 c.c. The solution need not be filtered, inasmuch as the volume of the insoluble matter seldom amounts to 0·05 c.c. Twenty-five c.c. of the solution are delivered into a four-ounce beaker and neutralized with ammonia—until a precipitate just begins to form—and then treated with 5 c.c. of nitric acid of 1·4 sp. gr. Ten c.c. of a saturated solution of ammonium nitrate are added, and the solution diluted to a volume of 50-75 c.c. It is then brought to a full boil, removed from the lamp, and 5 c.c. of the *aqueous* solution of ammonium molybdate added. This is followed by a second and a third 5 c.c. if necessary, the precipitate is allowed to settle, and filtered at once. It is washed thoroughly by decantation and on the filter. The filter and precipitate are transferred bodily to the beaker. Standard alkali is then run in, and at least 0·5 c.c. of a phenolphthalein solution (1 per cent.) added, then standard acid until the colour vanishes. Each c.c. of alkali equals one milligramme of P_2O_5.

A. G. B.

REVIEW.

THE MICRO-ORGANISMS OF FERMENTATION. By ALFRED JÖRGENSEN. London: Lyon. Price 10s.

The morphology and biology of the organisms concerned in the many varieties of fermentation, which occur naturally or are induced artificially, now possesses a wide and diffuse field of literature of its own. In the work before us, the author

has attempted to bring together, within fairly small compass, the salient points of this enormous mass of literature, and to give a general view of the subject in so far as it concerns the great fermentation industries. Working on these lines, he has succeeded in producing an exceedingly readable volume of handy size, which contains matter of the utmost interest to the chemist, biologist, and botanist. In the general arrangement of the work, the methods for the microscopical and biological examination of bacteria and yeast fungi are first described, this being followed by methods for the examination of air and water for such organisms. An account of the more commonly-occurring bacteria and mould fungi comes next. This is followed by a description of that numerous class of bodies—the alcoholic ferments—together with a short *résumé* of the various theories of fermentation, and this naturally forms the most important section of the work. An account is then given of the methods for the preparation of pure cultures of yeast on the principles first enunciated by Dr. Hansen, of the Carlsberg Laboratory. The last chapter is dedicated to a description of the beneficial results which have accrued in actual practice, where the principles, which have been gradually evolved during the last few years from our increased knowledge of the organisms of fermentation, have been applied. A list of the extensive bibliography of the subject concludes the work. The present volume, which is the second edition of the work in the English language, is a translation of the enlarged third German edition, and great credit is due to the translators, Dr. A. K. Miller and Mr. E. A. Lennholm, for the excellent manner in which they have performed their task. The book is well and clearly printed, neatly bound, and contains numerous illustrations. We can strongly recommend it as an indispensable manual to all those who are engaged in any of the industries where fermentation plays an important part. W. J. S.

CORRESPONDENCE.

To the Editors of THE ANALYST.

SIRS,—I am sorry to see that an allusion to raspberry-jam in my paper on Vinegar, recently read before the Society of Public Analysts, should have been misconstrued by Messrs. Allen and Hehner. My argument was, that where an identical result can be obtained by alternative methods, it is not the duty of the analyst to go behind the result.

As my thoughts have been previously misunderstood, perhaps I had better add that I don't look for the conversion of turnips into raspberries ; but if it were possible, I should consider the author of the process a public benefactor rather than a dishonest manufacturer.—Yours faithfully,

Stourport, February 21, 1894. EDWARD COLLENS.

To the Editors of THE ANALYST.

DEAR SIRS,—A sentence has, through a printer's error, crept into our paper on "The Leffmann-Beam Method," ANALYST, *this volume*, p. 68, lines 13 and 14 from bottom.

It was not in the original paper, but formed portions of a sentence on the wrapper used to keep the paper clean ; the sentence being incomplete, was not sense as it stood, and the printer made an effort to form readable English by putting in an "is" where we had written "as." This, though making the sentence read well, entirely altered its meaning, and seemingly commits us to a direct attack on the Babcock method. As will be seen in the previous portion of the paper, we have studiously avoided any reference to the Babcock process, which has not had for its object the elucidation of conditions of the Leffmann-Beam method.—Yours truly,

H. DROOP RICHMOND.

Bayswater, March 28, 1894. L. K. BOSELEY.